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71 Applicant:
BASF AG, 67063 Ludwigshafen, DE

72 Inventor:
Neumann, Hans-Peter, Dr. 67067
Ludwigshafen, DE; Walter, Marc, Dr.,
67227 Frankenthal, DE; Schulz, Ralf, Dr.,
67346 Speyer, DE; Heidemann, Thomas,
Dr., 69469 Weinheim, DE

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- 54 A method for the shut-down of an oligomerization reactor
- 57 A method for the shut-down of a reactor for the oligomerization of alkenes on a nickel-containing heterogeneous catalyst, for which the percentage content of alkene in the reactor feed is reduced with the help of a hydrocarbon flow that is almost free of aromates by reducing the percentage content of alkene in the reactor feed during the shut-down to less than 10% by weight of the total feed in such a manner that the catalyst temperature does not or only slightly exceed the maximum catalyst temperature during production and prior to the shut-down and in which case one partially or completely uses this flow as the hydrocarbon flow that is almost free of aromates and one retains when the oligomeric products are separated from the reactor discharge.

Description

[0001] This invention concerns a method for the shut-down of a reactor for the oligomerization of alkenes on a heterogeneous nickel-containing catalyst, for which one reduces the percentage content of alkene in the catalyst feed with the use of a hydrocarbon flow that is almost free of aromates.

[0002] Alkenes and particularly those with between 2 and 6 carbon atoms and their mixtures are available in large quantities from FCC units as well as from steam crackers. After separating the iso-butene, these alkenes are well suited for the production of oligomers, particularly of octenes and dodecenes. By way of a hydroformylation and subsequent hydration to form the respective alcohols, octenes as well as dodecenes can be used for the production of softening agents. In that regard, a particularly great demand exists for those "oxo-alcohols" that are available in that manner and exhibit a low degree of branching in the alkyl chain; this is indicated by a so-called low ISO index.

[0003] The oligomerization of alkenes with the above-mentioned carbon numbers on heterogeneous catalysts is discussed in Hydrocarbon Processing, February 1992, page 45/46. The use of heterogeneous nickel-containing catalysts is disclosed, for example, in the older German patent applications with file numbers 199 10 103.5 and 100 15 002 as well as in WO-A 99/25668; the expert already knows of such suitable catalysts from DE-A 43 39 713 and from the older German patent application with file number 199 57 173.3. Reference is hereby made to the full content of these documents for the execution of the oligomerization reaction.

[0004] During such processes, the service life ("time of exposure") of heterogeneous catalysts containing nickel is a function of their manufacturing method (see, for example, the older German patent application with file number 199 15 357.4) as well as of the oligomerization process type that is run in the stationary state (see WO-A 99/25668, for example).

[0005] However, the way in which one interrupts the conversion in the reactor prior to carrying-out maintenance work or in the case of operational problems has a great effect on the time of exposure exhibited by the catalyst. For such interruptions the conversion in the reactor is generally reduced in a controlled manner; the term "shut-down" is commonly applied to this situation.

[0006] The oligomerization of low-molecular alkenes is generally accompanied by a noticeable evolution of heat. Furthermore and with an adiabatic reaction type, practically the whole reaction heat is by way of the reaction mixture removed from the reactor during a reaction on a heterogeneous catalyst. This indicates that the reactor through-put and thus also the conversion per time unit depends on the amount of heat that must be removed from the reactor.

[0007] The catalyst activity level may be reduced in an irreversible manner particularly when shutting down an adiabatically operated oligomerization reactor, when this also causes peak temperatures in the catalyst bed. Furthermore, it is possible that undesirable high-boiling

oligomers are formed at such temperature peaks; they are deposited permanently on the catalyst surface and this will also lower the catalyst activity level.

[0008] US-A- 5,932,778 (BP) describes a process for the polymerization of olefins on a solid bed of an acid catalyst, in which the alkene-containing material flow is replaced with a flow that contains practically no alkenes and has an aromate percentage content of at least 5% by volume. This method is only partly suited for the shutting-down of reactors with heterogeneous nickel-containing solid catalyst beds, since the aromates form undesirable secondary products when the reactor is started-up again. Furthermore, such an aromate-containing material flow is not often easy to come by.

[0009] From US-A 4,996,383 (Philips) is known a method for the dimerization of alkenes, in which the reactor is shut-down by interrupting the alkene-containing supply flow and by supplying the reactor instead with an alkene-free flow consisting of C₂- to C₅-aliphates. However, such aliphate flows are also not easy to come by.

[0010] Accordingly, the task of this invention consists in the development of a method to shut-down such a reactor by lowering the alkene content in the reactor feed with the use of material flows that are easier to come by and whose components do not form any disturbing secondary products when the reactor is started-up again.

[0011] Accordingly, a method was found for the shut-down of a reactor for the oligomerization of alkenes on a heterogeneous nickel-containing catalyst, in which the alkene percentage content in the reactor feed is reduced with a hydrocarbon flow that is almost free of aromates, which is characterized by the fact that the alkene percentage content in the reactor feed is lowered in such a manner to less than 10% by weight of the total feed that the catalyst temperature does not or only slightly exceed the maximum catalyst temperature during production and prior to the shut-down, in which case one partially or completely uses that flow as the aromate-free hydrocarbon flow that is retained when the oligomeric products are separated from the reactor discharge.

[0012] Preferred examples of the method in accordance with the invention form the subject of the related patent claims.

[0013] In this document, "oligomers" are understood to include dimers, trimers and higher products of the joint depositing of the alkenes used here that - in the case of a reaction with alkene - have between 2 and 6, preferably up to 18, particularly preferred 12 and very much preferred 8 carbon atoms.

[0014] In the production area and prior to the shut-down in accordance with the invention, an application flow (hereinafter called "feed") is generally run continuously in the reactor for the oligomerization (hereinafter called "reactor") and has an alkene percentage content of between 10 and 100% by weight and preferably between 40 and 70% by weight.

[0015] Establishing the composition of the feed is not often based on the fact alone that the reactor receives a sufficient alkene quantity for the reaction on the catalyst. The expert is generally faced with the task to ensure a sufficient heat removal from the reactor and to thus maintain the extent of

the feed flow, possibly expressed by its volume. In that manner, it is also possible to keep alkene exposure time in the reactor within close limits. It is possible that a longer exposure time can increase the alkene reaction with a corresponding heat development and can lead to an undesirable temperature increase on the catalyst.

[0016] The feed may particularly consist of a fresh flow that has a high alkene content and a flow with a low alkene content after the oligomeric products were separated from the reaction discharge. In practical applications, the percentage contents of the flow with a high alkene content and the flow with a low alkene content at the feed of the production area shall be adjusted such that the alkene content remains the same in the feed. A percentage content of the flow with little alkene that is too high would - at a constant feed volume - reduce the alkene percentage content in the feed and this is basically not desirable in the production area.

[0017] In this regard, the shut-down of the reactor is understood to be the process, in which the alkene percentage content in the feed is in a targeted manner reduced to between 0 and 10% by weight, preferably between 1 and 5% by weight and particularly between 3 and 5% by weight of the total feed.

[0018] With respect to the shut-down, it is of great importance that the temperature in the main catalyst quantity and preferably in the whole catalyst does not exceed the maximum catalyst temperature or exceed it only by little in the production area and prior to the shut-down, i.e., preferably by not more than 20 °C, particularly preferred by not more than 10 °C and very much preferred by not more than 5 °C. However, a temperature lower than the maximum temperature is not critical; this generally lowers the reaction rate on the catalyst and this is normally not desired.

[0019] According to the above, the catalyst temperature during the oligomerization considered here can be controlled with the following factors:

1. Feed temperature
2. Heating or cooling the reactor
3. Setting the alkene content in the feed
4. Feed volume

[0020] Prior to supplying the material to the reactor and for that purpose, the temperature of each individual partial flow or the completely mixed feed can be adjusted with generally known devices such as heat exchangers.

[0021] Accordingly and with the above-mentioned measures, the expert has at his disposal a flexible array of methods to meet the catalyst temperature requirements when the reactor is to be shut-down. Since these are generally known operations used in the chemical processing technology, there is no need to explain their execution here.

[0022] Since the alkene percentage content in the feed is lowered in accordance with the invention during the shut-down and since it is not economical to prepare many feeds with different alkene contents, it is appropriate to prepare the respective desired feed composition by mixing the respective quantities of suitable flows with different alkene contents. Such a mixing process is

routinely carried-out by an expert and there is thus no need for explanations. In that connection, the expert performs a few initial tests to determine the ratio between the flow with a high alkene content and the diluting flow with a low alkene content in view of the desired selectivity levels in the production area.

[0023] Flows to be mixed to form suitable feeds that consist of alkene exclusively or have a high alkene percentage content may consist of the respective pure alkenes such as propene, 1-butene, 2-butene, iso-butene, 1-pentene, 2-pentene, the methyl butenes 1-hexene, 2-hexene, 3-hexene, the methyl pentenes as well as mixtures of two or several of these alkenes. Also suitable are mixtures of one or several of these alkenes with alkane. Suitable alkanes are butanes such as n-butane, iso-butane, pentanes such as n-pentane, the methyl butanes, n-hexane and the methyl pentanes. Preference is hereby given to mixtures of alkenes with alkanes, in which case the alkenes and alkanes in particular have 4 carbon atoms each.

Butane	10 to 90% by weight
Butene	10 to 90% by weight

in which case the butene fraction may have the following composition, for example:

1-butene	1.0 to 50% by weight
cis-2-butene	1.0 to 50% by weight
trans-2-butene	1.0 to 99% by weight
iso-butene	0.1 to 5% by weight

[0024] Particular preference is given to the use of the so-called Raffinate II. This is a butene-containing C₄-hydrocarbon mixture as obtained from the C₄-section of crackers, i.e., after the separation of higher unsaturated hydrocarbons such as dialkene and particularly 1,3-butadiene or acetylene and the subsequent separation of iso-butene. The following is an example of a typical composition for a Raffinate II:

iso- and n-butane	26% by weight
iso-butene	1% by weight
1-butene	26% by weight
trans-2-butene	31% by weight
cis-2-butene	16% by weight

[0025] To dilute the flow with a high alkene content down to the desired alkene content in the feed for the production area, one preferably uses the reactor discharge component that remains after the oligomeric products are separated.

[0026] To obtain this reactor discharge component, one separates the reactor discharge - preferably by distillation - into oligomeric products removed at or near the column sump and volatile components taken at the column head (as "head flow"). Such a head flow exhibits the following typical composition:

Alkene	30 to 80% by weight
Alkane	20 to 70% by weight

[0027] The above thoughts regarding a sufficient heat dissipation from the reactor and the thus required extent of the feed flow also apply to the shut-down period. During shut-down exists the special situation that the feed flow can be reduced accordingly when the alkene content in the feed decreases during the shut-down and thus decreases the heat development in the reactor. This is generally done only in the case this does not lead to a longer time of exposure of the alkene on the catalyst.

[0028] In the case of this invention, it was found that the different feeds of equal volume are capable of transporting the same reaction heat quantity from the reactor. Feed/volume differences of $\pm 10\%$ and particularly of $\pm 5\%$ have generally no noticeable negative effect on product quality and catalyst activity level after starting-up the reactor again.

[0029] In accordance with the invention, the decrease in the volume percentage content of alkene in the feed is partially or completely made up by supplying a hydrocarbon flow that contains almost no aromates and preferably and mainly contains one or several alkanes and - if desired - one or several alkenes, and that preferably and mainly consists of the reactor discharge percentage content that remains after the oligomeric products have been separated.

[0030] Within the scope of the invention, the hydrocarbon flow that is almost free of aromates preferably contains less than 1% by weight and particularly preferred less than 0.5% by weight of aromatic compounds.

[0031] In a particularly preferred example of the method in accordance with the invention, 60 to 100% by weight, preferably 85 to 100% by weight and particularly preferred 100% by weight of the reactor discharge components that remain after the oligomeric products have been separated are piped back to the feed.

[0032] In a preferred manner and during the shut-down, the percentage content of the flow or flows with a high alkene content are reduced at the feed and the thus caused reduction in the feed volume is made up partially or completely with a hydrocarbon flow that contains almost no aromates, that preferably and mainly consists of one or several alkanes and - if desired - of one or several alkenes, and that preferably and mainly consists of the reactor discharge component that remains after the oligomeric products have been separated.

[0033] In a particularly preferred manner, the feed volume decrease associated with reducing the percentage content of alkene is made up with the head flow obtained from a processing by distillation of the reactor discharge. Furthermore, this can be achieved with another hydrocarbon flow that contains almost no aromates and preferably and mainly consists of one or several alkanes and - if desired - of one or several alkenes such as the above-mentioned Raffinate II or the so-called Raffinate III that is also easily available on a large scale and has the following composition:

n- and iso-butane	85.0 to 99.8% by weight
iso-butene	0.1 to 5.0% by weight

n-butene

0.1 to 10.0% by weight

[0034] As for the rest and prior to using the feed, butadiene, sulfur-containing compounds and oxygen-containing compounds such as alcohols, aldehydes, ketones or ethers can be removed from the feed through a hydration or absorption on a molecular sieve.

[0035] The feed supply to the reactor can be achieved by piping the flows to be mixed simultaneously and individually to the reactor - possibly through separate pipes - or after a prior mixing.

[0036] To prevent a decrease in the reactor temperature due to the reduced alkene reaction during shut-down, a particularly preferred example of the method in accordance with the invention ensures that the catalyst temperature is lower than the temperature in the production area prior to the shut-down by not less than 10 °C and particularly by not less than 5 °C. Accordingly and in practical applications, the reactor temperature or the temperature of the feeds or partial flows from which the feed may be prepared immediately prior to the reaction, is increased during the shut-down in such a manner that the catalyst temperature does not exceed or does exceed by little the maximum catalyst temperature during the production and prior to the shut-down. That is approximately the case when the feed outlet temperature from the reactor during the shut-down is equal to the reactor outlet temperature or is almost equal to the reactor outlet temperature during production.

[0037] In another preferred example of the method in accordance with the invention, the whole head flow of the column used for the distillation of the reactor discharge is right from the start of the shut-down returned to the reactor and the reactor temperature is right from the beginning increased by 1 to 5 °C and preferably by approx. 2 °C.

[0038] Above all, the shut-down duration is a function of the catalyst type and of the dimensions of the solid catalyst bed. It normally requires between 1 and 40 hours and preferably between 10 and 20 hours.

[0039] In a preferred manner, the alkene percentage content is decreased continuously during the shut-down, i.e., in equal increments to a value of less than 10% by weight.

[0040] As for the rest, the reactor discharge composition can be analyzed in a generally known manner and particularly by way of a gas chromatography.

[0041] The feed flow to the reactor is normally interrupted at the end of the shut-down and the reactor temperature is allowed to decrease to a temperature of between ambient temperature, this is normally a temperature of between 20 and 25 °C, and 40 °C. However, the reactor pressure is generally maintained at the same level when interrupting the reactor operation and the feed remaining in the reactor generally remains in the condensed state until the reactor is started-up again.

[0042] During the interruption of its operation that may last between several days and several weeks, the reactor may be left in the state results from the shut-down and subsequent cooling.

[0043] It could be shown that the reactor does not suffer a significant activity loss during its cooling period and during the period leading to the new reactor start, i.e., when the reactor is shut-down previously according to the invention.

[0044] The method in accordance with the invention is preferably used for the oligomerization of alkenes with between 2 and 6 carbon atoms on oligomerization catalysts that contain nickel (hereinafter called "Ni-catalysts").

[0045] Above all, Ni-catalysts may consist of those nickel-containing catalysts that are known to have a minor oligomer-branching effect: See, for example, Catalysis Today, 6, 329 (1990), particularly pages 336-338, as well as the references listed in WO-A 95/14647 and in the older German patent application with file number 199 57 173.2 regarding prior art, in which case reference is made here explicitly regarding the catalysts.

[0046] The following can be listed as Ni-catalysts samples in which the nickel generally occurs in the oxidic form:

- Nickel on silicon dioxide,
- Nickel on silicon dioxide-aluminum oxide,
- Nickel on silicon dioxide-aluminum oxide-layer silicates such as mica and oxides of aluminum, particularly montmorillonite,
- Nickel on zeolite carriers such as mordenite, faujasite, zeolite X, zeolite Y, zeolite ZSM-5 or other zeolites of the ZSM-type, zeolites with a MCM-41 structure or CZS-1 structure,
- Nickel on aluminum oxide, possibly together with anion of particularly inorganic acids such as sulfuric, phosphoric and boric acid,
- Nickel on zirconium oxide that has been treated with acids such as sulfuric acid, phosphoric acid or boric acid,
- NiO/ZrO₂/SO₄/SiO₂-systems,
- Nickel on sulfated titanium oxide.

[0047] According to a preferred example of the method in accordance with the invention, the oligomerization is performed in the liquid phase and with the use of the Ni-catalysts described and claimed in WO-A 95/14647 and in the older German patent application with file number 199 57 173.2. Reference is made here explicitly to these documents and their information regarding method and Ni-catalysts is considered incorporated here.

[0048] The catalytically active mass of the Ni-catalysts described in WO-A 95/14647 basically consist of nickel oxide, silicon oxide, titanium oxide and/or zirconium oxide and possibly of aluminum oxide, i.e., without considering contaminants that were introduced through initial or process chemicals during the production of the Ni-catalysts. These Ni-catalysts contain between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium oxide and/or zirconium oxide, between 0 and 20% by weight aluminum oxide and the rest to reach 100% by weight consists of silicon dioxide. This is obtained by precipitating the Ni-catalysts at pH 5-9 by adding an aqueous solution that contains nickel nitrate to an alkali water glass solution that still contains

titanium and/or zircon dioxide. The thus obtained Ni-catalyst mass is then filtered, dried and tempered at between 350 and 650 °C.

[0049] The Ni-catalysts described in the older German patent application with file number 199 57 173.2 generally consist of aluminum oxide that was coated with a nickel compound or a sulfur compound, in which case the finished Ni-catalyst exhibits a ratio between sulfur and nickel of 0.25:1 to 0.38:1.

[0050] The Ni-catalysts used in accordance with the invention are preferably arranged on a solid bed and thus consist of solid pieces such as tablets (5 mm x 5 mm, 5 mm x 3 mm, 3 mm x 3 mm), rings (7 mm x 7 mm x 3 mm, 5 mm x 5 mm x 2 mm, 5 mm x 2 mm x 2 mm) or strands or star strands (1.5 mm diameter, 3 mm diameter, 5 mm diameter). The above sizes and body types represent just examples and do in no way restrict the object of this invention.

[0051] When the Ni-catalyst is arranged on several solid beds in the reactor, the feed system can be divided and supplied to the reactor at several points such as before a first solid bed in the flow direction of the reaction mixture and/or between individual solid Ni-catalyst beds. When using a reactor cascade, for example, it is possible to supply the whole feed to the first reactor of the cascade or to supply it through several pipes to the individual cascade reactors as is described for the case of a single reactor.

[0052] The oligomerization reaction is generally run at temperatures of between 30 and 280 °C, preferably of between 30 and 140 °C and particularly preferred of between 40 and 130 °C and at a pressure of generally between 1 and 300 bar, preferably of between 5 and 100 bar and particularly preferred of between 10 and 50 bar. The pressure is selected appropriately in such a manner that the feed is present in an above-critical manner and in the liquid state at the adjusted temperature.

[0053] The reactor generally consists of a cylindrical reactor in which the Ni-catalyst is placed; as an alternative, it is also possible to use a cascade with several and preferably two such reactor arranged in series.

[0054] The Ni-catalyst can be arranged on a single or on several solid N-catalyst beds in the reactor or in individual reactors. Although it is preferred to use the same Ni-catalysts in all reactors of the cascade, it is also possible to use different Ni-catalysts in the individual reactors of the cascade.

[0055] Furthermore, different reaction conditions with respect to pressure and/or temperature within the above-mentioned pressure and temperature ranges can be set in the individual reactors of the reactor cascade.

[0056] The liquid feed may pass, for example, from the top to the bottom through the solid Ni-catalyst bed in the reactor or reactor cascade.

[0057] From a technical point of view, an adiabatic reaction or operation refers to a reaction or operation, in which the whole reaction heat is absorbed by the reaction mixture and is discharged with it from the reactor, i.e., with the exception of the part of the reaction heat that is transferred to the outside through a natural heat conduction and heat dissipation process.

[0058] From a technical point of view and in contrast to the above, an isothermal reaction or operation forces the removal of the reaction heat from the reactor with cooling and thermostat devices in a targeted manner and in addition to the natural heat conduction and dissipation process. In that regard, it is practically impossible to avoid that a - negligibly small - part of the reaction heat is transferred outward with the reaction mixture.

[0059] As an alternative to the solid bed reactors, the process in accordance with the invention can also be run in other reactors that are known to the expert to be suitable for such heterogeneously catalyzed reactions such as stirrer tanks or loop-type bubble reactors (see M. Baerns, H. Hoffmann, A. Renken, Chemical Reaction Technology, Thieme Verlag, Stuttgart 1987, page 237 and following).

[0060] In such processes, the conversion rate to form oligomers generally varies between 10% and 100% and preferably between 50% and 100% in relation to the alkene used in the reaction.

Examples

A) Equipment

[0061] Figure 1 shows a schematic representation of a device used to run the process in accordance with the invention continuously at 30 bar. Raffinate II as the flow with a high alkene content is piped through F to the partial adiabatic reactor R1 and from there and by way of an intermediate cooling unit ZK piped to the partial adiabatic reactor R2. The partial reactors are 4 m long and their diameter is 0.8 m. The discharge from reactor R2 is processed in column K by distillation and the oligomeric product is removed as a sump product through B. The head flow of column K is partially or completely - as desired - returned through Z to reactor R1, in which case the remaining part of the head flow is through P (as "purge" flow) transferred outward in the case of a partial return. It is possible to introduce an alkene-poor flow through S.

Material flows supplied from the outside

B.1 Flow with high alkene content (See Fig. 1: Supply through F)

[0062] A Raffinate II of the following composition was used:

iso-butane	2% by weight
n-butane	10% by weight
iso-butene	2% by weight
1-butene	32% by weight
trans-2-butene	37% by weight
cis-2-butene	17% by weight

B.2) Other flow with low alkene content (See Fig. 1: Supply through S)

[0063] A Raffinate III of the following composition was used:

n- and iso-butane	89.8% by weight
iso-butene	4.6% by weight
n-butene	5.6% by weight

C) Catalyst

[0064] A material with the following composition served as the catalyst:

NiO	50.0% by weight
TiO ₂	12.5% by weight
SiO ₂	33.5% by weight
Al ₂ O ₃	4.0% by weight

[0065] Used in the form of tablets measuring 5 mm x 5 mm and prepared analogous to example 2 in DE-A 43 39 713.

D) Oligomerizations

[0066] A series of two tests in accordance with the invention and a reference test were run one after the other in the equipment described in (A). To do so, a stationary state of oligomerization was initially set in the two reactors R1 and R2. Reactors R1 and R2 were then shut-down simultaneously. The composition of the reaction mixture from reactor R2 was monitored by way of gas chromatography. From the very beginning and for the whole shut-down period, the head flow from column K was in all cases completely and by way of Z returned to the reaction. The inlet and outlet temperatures of the reaction mixture were measured at the reactors. After their shut-down, reactors R1 and R2 were allowed to cool to 30 °C and they were then started-up again (see Table 1).

[0067] The feed was mixed using Raffinate II, the returned part of head flow Z from column K and possibly Raffinate III to achieve the desired composition in such a manner that the feed always had the same volume.

Phase I: Setting the initial stationary state

[0068] The Raffinate II supply was set at $0.375 \text{ kg/l}_{\text{catalyst}} \times \text{h}$ at a weight ratio of 1:3 between the Raffinate II and in relation to the head flow part that contained less alkene and was supplied through Z.

Phase II: Reactor shut-down in accordance with the invention

[0069] The percentage content of Raffinate II in the feed flow was set such that it was equal to the percentage content by weight of the continuously produced oligomers that were then transferred

outward. Accordingly, the Raffinate II functioned as a "make up flow" for the decreasing volume of the reactor discharge in relation to the feed and on the basis of outward transfers (through P and in the form of the oligomeric products). In that regard, the ratio between the Raffinate II and the head flow that contained less alkene and was supplied through Z dropped to less than 1:3. The temperature at the inlet of reactors R1 and R2 was increased to accelerate the shut-down process (see Table 1). As the last step, both reactors were cooled to 30 °C and were then started-up again.

Phase III: Reactor shut-down in accordance with the invention

[0070] The Raffinate II feed flow to the reactor was interrupted and Raffinate III was introduced as the make up flow. As the last step, both reactors were cooled to 30 °C and were then started-up again.

Phase IV: Reference test (shut-down without a make up flow)

[0071] The Raffinate II feed flow to the reactor was interrupted. However, the thus created volume decrease in the feed flow with respect to the stationary operation was not made up. As the last step, both reactors were cooled to 30 °C and were then started-up again.

[0072] Test results show that the catalyst experienced an activity drop when no make up flow was added during the shut-down. This undesirable effect was compensated by operating the reactors at higher temperatures when starting them up again. This was the only way to achieve yields, conversion rates and selectivity levels that were at the original levels.

[0073] In contrast to the above, no drop in the catalyst activity level occurred when the shut-down was performed in accordance with the invention.

[0074] The terms in Table 1 have the following meaning:

- ET1 Inlet temperature at reactor R1 [°C]
- AT1 Outlet temperature at reactor R1 [°C]
- ET2 Inlet temperature at reactor R2 [°C]
- AT2 Outlet temperature at reactor R2 [°C]
- Temperature change during shut-down
- Oligo Oligomer percentage content in relation to discharge weight [%]
- U Butene yield [%]
- S Selectivity: Percentage content of C₈-isomers on the formed oligomers [%]
- 1) Corresponding to percentage content by weight of the formed and then separated oligomers.
- 2) Not determined.

Table 1

		Raffinate II / Absolute supply quantity [kg/l _{catalyst} *h Raffinate II]	Supply quantity relative to the flow containing less alkene [% by weight / % by weight]	Make up flow during shut-down	ET1 [°C]	AT1 [°C]	ET2 [°C]	AT2 [°C]	Oligo [%]	U [%]	S [%]
Phase I	Stationary operation I after start-up	0.375	1 : 3	-	38	67	60	75	18.3	83.1	83.3
Phase II	Shut-down II	1)	< 1 : 3	Raffinate II	→55	→60	→70	→70	2)	2)	2)
	Stationary operation II after start-up	0.375			37	67	60	74	18.7	82.7	83.5
Phase III	Shut-down III	0	1 : 3	Raffinate III	38	67	60	75	2)	2)	2)
	Stationary operation III after start-up	0.375			39	68	60	76	18.4	83.2	83.1
Phase IV (Reference)	Shut-down IV	0	1 : 3	Without	38	→103	60	→76	2)	2)	2)
	Stationary operation IV after start-up	0.375			59	87	70	87	18.6	83.5	82

Patent claims

1. A method for the shut-down of a reactor used for the oligomerization of alkenes on a heterogeneous nickel-containing catalyst, for which the alkene percentage content in the reactor feed is lowered with the help of a hydrocarbon flow that contains almost no aromates, **characterized by the fact that** the alkene percentage content in the reactor feed is reduced to 10% by weight of the whole feed in such a manner that the catalyst temperature does not exceed or only slightly exceeds the maximum catalyst temperature during production and prior to the shut-down, in which case one partially or completely uses that flow as the hydrocarbon flow with almost no alkenes that is retained when the oligomeric products are separated from the reactor discharge.
2. A method in accordance with claim 1, characterized by the fact that one continues to use a hydrocarbon flow that contains almost no aromates and mostly consists of one or several alkanes and of one or several alkenes, if so desired.
3. A method in accordance with claim 1 or 2, characterized by the fact that one uses Raffinate II as the other hydrocarbon flow that is almost free of aromates and consists mainly of one or several alkanes and of one or several alkenes, if so desired.
4. A method in accordance with one of claims 1 through 3, characterized by the fact that one uses Raffinate III as the other hydrocarbon flow that is almost free of aromates and consists mainly of one or several alkanes and of one or several alkenes, if so desired.
5. A method in accordance with claims 1 through 4, characterized by the fact that the percentage content of the reactor discharge that one retains when separating the oligomeric products from the reactor discharge is completely returned to the reactor.
6. A method in accordance with claims 1 through 5, characterized by the fact that one generally maintains the feed volume to the reactor in relation to the feed volume in the upstream production area when shutting-down the reactor.
7. A method in accordance with claims 1 through 6, characterized by the fact that the reactor feed will exhibit at a certain point in time and during the shut-down a percentage content by volume of Raffinate II that is equal to the percentage content by volume of the oligomeric products that are separated from the reactor discharge at or approximately at the same point in time.

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Figure 1